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Biodiesel Synthesis over Mesoporous Solid Acid Catalyst

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Abstract

A simple and a new hydrothermal method is adopted for the synthesis of $CuAlPO_4$ and $MgAlPO_4$ catalyst by using Triethylamine as a template. The synthesized catalysts are characterized by using FT-IR, XRD, SEM and BET. These characterization techniques are proved the formation of tetrahedral framework of $CuAlPO_4$ and $MgAlPO_4$ catalyst. The biodiesel synthesis reaction has been carried out with ethanol. The experimental conditions like contact time, temperature, mole ratio, catalyst dosage are optimized for maximum conversion. Conversion of biodiesel and selectivity of biodiesel is more on $CuAlPO_4$ than $MgAlPO_4$.

Keywords: *Biodiesel; Characerization; New technique; Solid acid.*

1. INTRODUCTION

Biodiesel is an alternative source among the petroleum fuel field. It can be used in diesel engine without much changes. Easy biodegradability of biodiesel is also one of it benefit. Generally, Biodiesel are less poisonous compared to the ordinary diesel. Therefore, in current years, research depends on the plant-based fuels. Diffenent varieties of plant based oils have been involved in the biodiesel synthesis such as canola, Jatropha, palm kernel, sunflower and palm (Wilson, 2007). Among the oils, we take Jatropha oil for our study. Catalysts used in biodiesel synthesis such as homogeneous and heterogenous are reported in the literature (Subrahmanyam *et al.* 2003). Current research based on the application of heterogeneous catalysts to produce biodiesel, because of the ecofriendly and economical benefits (Elangovan *et al.* 1998). The surfactant molecules are used as the important templates in the production of meso structured molecular sieves with the cubic or hexagonal ordering of pore system (Tatsuo Kimura, 2005). Moreover, the surfactant molecules cause environmental pollution and corrosion (Jing Yu *et al.* 2007). To solve all these problems with beneficial and eco friendly, an attempt has been made to produce mesoporous aluminophosphate molecular sieves with minimum expense (Selvam and Mohapatra, 2006). In the recent investigation, $AlPO_4$ based heterogeneous catalyst are applied for transesterification reaction. For this purpose, a new nanoporous solid acid $AlPO_4$ has been prepared by using triethylamine as a template. The triethylamine is reported for the preparation of microporous $AlPO_4$ based materials (Cheralathan *et al.* 2000). In the present investigation, triethylamine is used for the preparation of mesoporous alumino phosphate molecular sieve by adopting a simple hydrothermal method without using the autoclave.

2. EXPERIMENTAL METHODOLOGY

2.1 Materials

The chemicals for the synthesis of Mesoporous aluminophosphate are Aluminium hydroxide and Phosphoric acid. The metal sulphates utilized for the isomorphous substitution in the $AlPO_4$ framework are $MgSO_4$, $CuSO_4$ respectively. Castor oil and ethanol are employed for the transesterification reaction. The catalysts used for the reaction are $MgAlPO_4$ and $CuAlPO_4$.

2.2 Methods

Mesoporous Alumino Phosphate is prepared by using Triethylamine as a template by simple synthesis method with the following gel composition 0.98 Al_2O_3 :

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P_2O_5: 0.02 MO: $(C_2H_5)_3N$: $300H_2O$. 7.8 g of Aluminium Hydroxide is dissolved in 7° ml of water and added slowly into the template (Triethylamine) solution and stirring it for 1h. Phosphoric acid is dissolved with 25 ml of water . Then the $CuSO_4$ and $MgSO_4$ added in the two separate synthesis of $CuAlPO_4$ and $MgAlPO_4$. The concentration of metal ion is 0.02M is added to the above mixture and stirred continuously for 2h to achieve homogenous mixture. Then the resulting gel is heated and dried in hot plate at 120 °C in open air and thoroughly washed with deionised water. The Solid is then filtered, dried, calcinated at 400 °C for 6hr to remove the organic template.

2.3 Characterisation

Various techniques have been used for the characterisation of the $AlPO_4$. It includes FT-IR, XRD, Surface area and pore size distribution and SEM. Fourier transforms infra red (FTIR) spectra of Mesoporous $AlPO_4$ is recorded in a Jasco FTIR-41° spectrophotometer in the range of 4000 - 400cm^{-1} using KBr pellet techniques. The formation of Mesoporous in $AlPO_4$ based molecular sieves are studied by powder XRD. X-ray diffraction (XRD) patterns are recorded on a Simanzu 600° diffractometer using Cu-Kα radiation (λ=1.5406 A^O) with the voltage 30kV and 3° mA at room temperature with the scanning rate of 0.5 degree per minute. Nitrogen adsorption-desorption measurements are made by using a Micromeritics ASAP 202° V3.0° H instruments, the sample is out gassed at 200 °C for 1hour. The surface areas and the pore size of the samples are obtained by the Brunauer-Emmett Teller (BET) method. Electron diffraction studies (SEM and TEM) are used to determine the morphology of Mesoporous $AlPO_4$ based materials. The Scanning Electron Microscope (SEM) images are recorded on a JEOL EO JSM-6390.

2.4 Catalytic reactor

Generally catalytic activities are carried out in both liquid and vapour phase. The liquid phase transesterification of castor oil with ethanol is carried out in a three necked RB flask with a condenser and a thermometer as shown in *Fig.*1. The weighed amount of ethanol, castor oil and calcined $CuAlPO_4$ and $MgAlPO_4$ based catalysts are added and allowed to stir for required time.

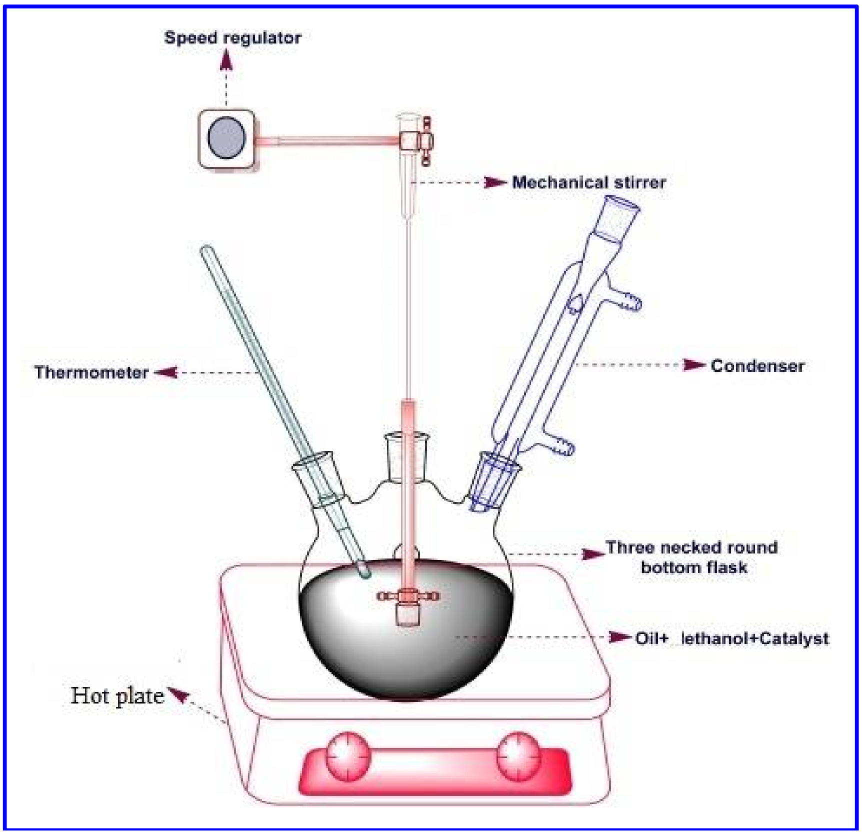

Fig. 1: Reactor setup for biodiesel synthesis

3. RESULT & DISCUSSION

3.1 Characterisation of $AlPO_4$ based molecular sieves

Characterisation techniques are essential to confirm the formation of tetrahedral structure, crystalline nature, surface area and pore size and its morphology.

FT-IR

The FT-IR spectra of as-synthesised and calcined Mesoporous $AlPO_4$ based materials such as $CuAlPO_4$, $MgAlPO_4$ are shown in below *Fig*. (a, b, c and d). These f*ig*.2 (a, b, c &d) are shown the strong and broad band at 3,450 cm^{-1} to 3,550 cm^{-1} which is assigned to the O-H vibration of water molecules that present in both as-synthesised sample. But in calcinated sample the strong –OH band becomes weak. The complete removal of the template is confirmed by the absence of characteristic C-H stretching bands at 2300 cm^{-1} to 2350 cm^{-1} as well as C-H deformation bands around 1630 cm^{-1} to 1650 cm^{-1}. The strong band at 1073 cm^{-1} is ascribed to the asymmetric stretching mode of tetrahedral $AlPO_4$. The Corresponding symmetric stretching is observed at 670 cm^{-1} to 885 cm^{-1} for both as-synthesised and calcinated sample of $CuAlPO_4$ and $MgAlPO_4$ **(**Campelo et al. 2003; 1986; Vijayasankar et al. 2010**)**. The bending mode is positioned near 480 cm^{-1} to 530 cm^{-1} for both samples.

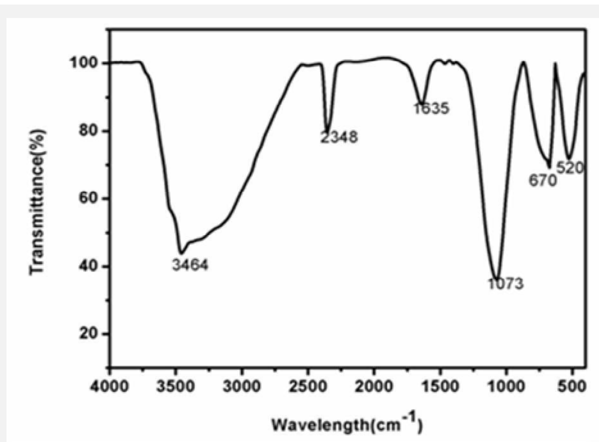

Fig. 2a: as-synthesised $CuAlPO_4$

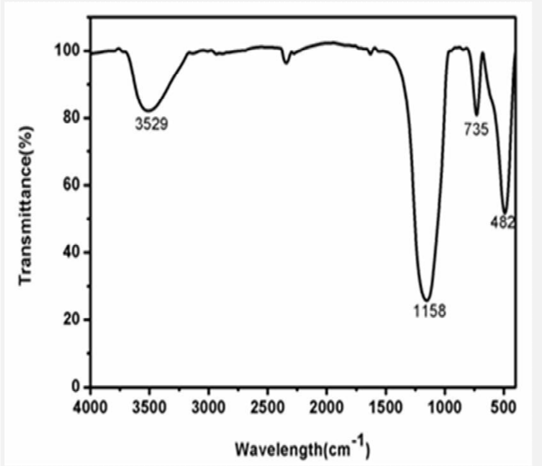

Fig. 2b: calcinated $CuAlPO_4$

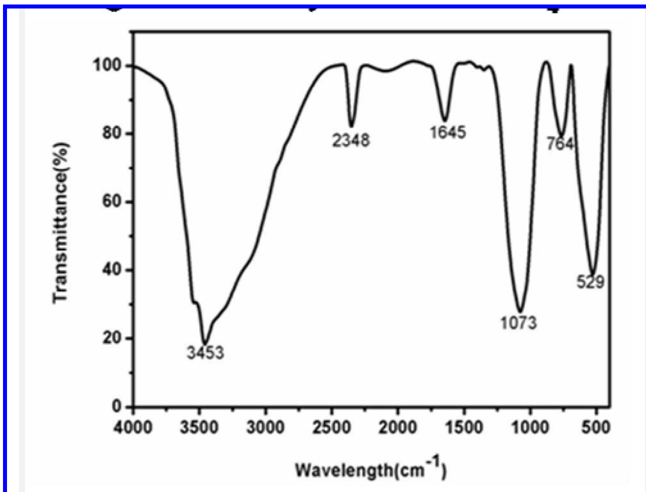

Fig. 2c: as-synthesised $MgAlPO_4$

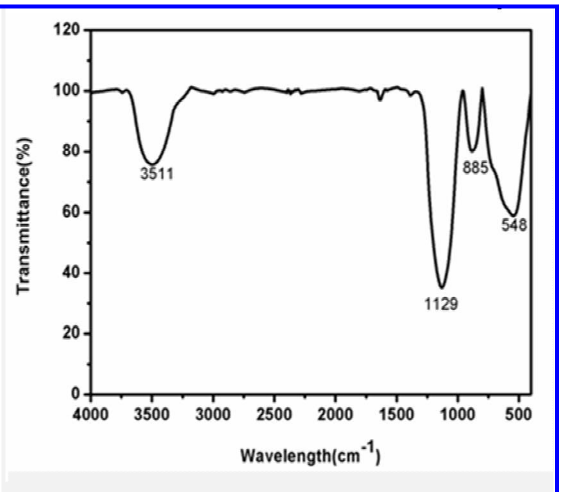

Fig. 2d: calcinated $MgAlPO_4$

X-Ray diffraction

The powder XRD analysis has been carried out for calcinated $MAlPO_4$ materials (fig. 3a & 3b). The XRD pattern of calcined $CuAlPO_4$ has high intense peak at $2\Theta = 21.61^o$ with the d-spacing of 0.41nm which proved the well crystalline nature of the material. Similarly, the XRD pattern of calcined $MgAlPO_4$ has high intense peak at $2\Theta = 66.96^o$ with the d-spacing of 0.13nm shows high intense reflection. The XRD datas are given in the following Table 1.

Table 1. XRD data for $CuAlPO_4$ and $MgAlPO_4$

Metal ion	Ionic Radii	JC-PDF No	Crystal system	Crystal Lattice
iCu^{2+}	0.56	881680	Hexagonal	Primitive
Mg^{2+}	0.54	881680	Hexagonal	Primitive

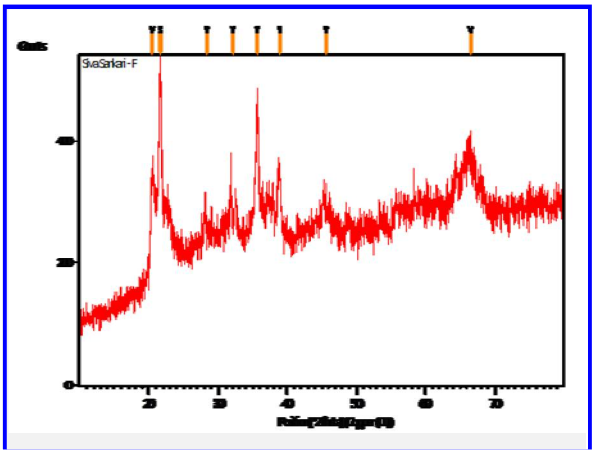

Fig. 3a: XRD pattern of $CuAiPO_4$

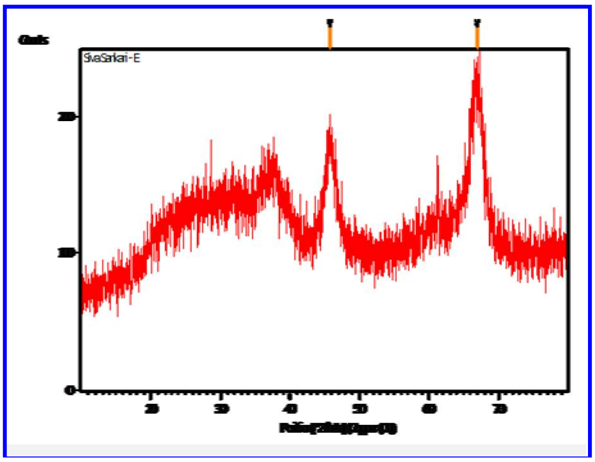

Fig. 3b: XRD pattern of $MgAiPO_4$

N_2 adsorption and desorption isotherm

The BET surface area and porevolume of the $CuAlPO_4$ are found as $30.13m^2/g$ and 0.034 respectively. The pore diameter of $CuAlPO_4$ are 4.47 nm. Then the BET suface area and pore volume of $MgAlPO_4$ are 71.4° m^2/g and 0.111 respectively. Pore diameter for $MgAlPO_4$ are 6.21nm. The datas are proved that $CuAlPO_4$ and $MgAlPO_4$ are Mesoporous molecular sieves.

Scanning electron microscopy

The morphology of the calcined $CuAlPO_4$and $MgAlPO_4$ are studied by SEM analysis shown in f*ig*. 4a and 4b. SEM images clearly represented the crystalline nature of metal ions incorporated $AlPO_4$ materials. Both materials have varied particle sizes in nano scale. Eventhough, these materials are synthesised by the same synthesis procedure, the morphology of the $CuAlPO_4$ and $MgAlPO_4$ are slightly varied . Morphological change of the $CuAlPO_4$ and $MgAlPO_4$ is with respect to the metal ion incorporation in the tetrahedral framework of the materials (Melo et al. 1999). It is an evidence for the metal ion incorporation in the tetrahedral framework of $AlPO_{4.}$

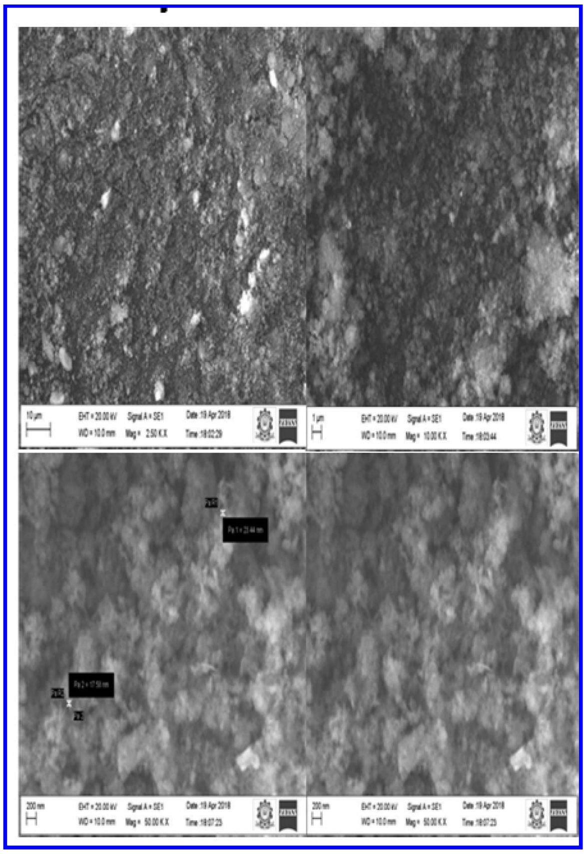

Fig. 4a: SEM Micrograph $CuAIPO_4$

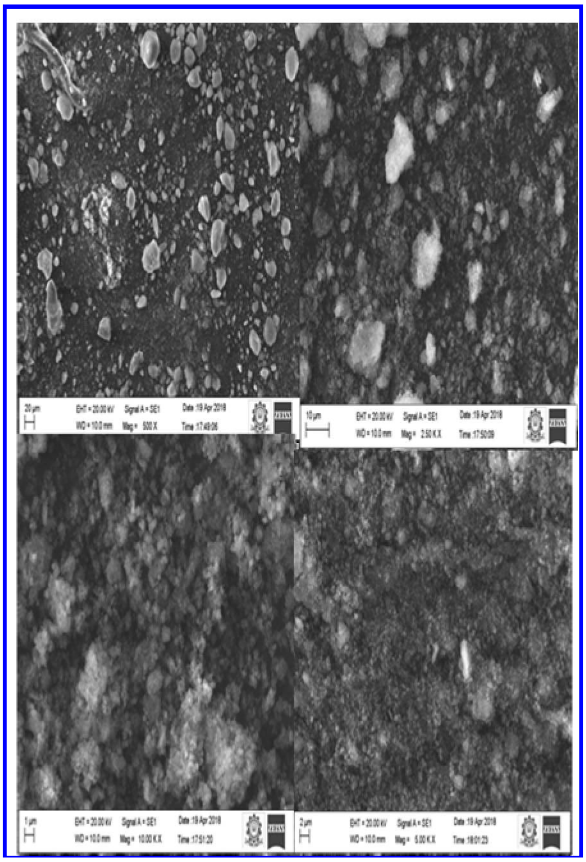

Fig. 4b: SEM Micrograph $CuAlPO_4$

4. TRANSESTERIFICATION OF CASTOR OIL WITH ETHANOL OVER MESOPOROUS $ALPO_4$ BASED

Molecular sieves

Transesterification of castor oil with ethanol has been carried out over $MAlPO_4$ as catalyst in liquid phase. The experimental conditions like effect of contact time, temperature, catalyst dosage, molar ratio are determined for maximum conversion and selectivity of the reaction.

4.1 Effect of contact time

The effect of contact time has been carried out by the transesterification of castor oil with ethanol over both the catalyst of $CuAlPO_4$ and $MgAlPO_4$. Table 2 & 3 and *Fig.* 5 shows the effect of contact time on transesterification reactions over $CuAlPO_4$ and $MgAlPO_4$ upto 4hr. The percentage of conversion of ethanol increases up to 2h for $CuAlPO_4$ and 3h for $MgAlPO_4$ and further increased of time decreases the conversion. The product formed in this reaction is biodiesel, glycerol and diethyl ether.

The selectivity of biodiesel over $CuAlPO_4$ is 81% and $MgAlPO_4$ is 44%. The Cu^{2+}ion present in the tetrahedral framework of the catalyst promote the maximum transesterification reaction than the Mg^{2+}ion.

Table 2. Effect of contact time on biodiesel synthesis over $CuAlPO_4$

Time (hr)	Conversion (%)	Selectivity (%)		
		Biodiesel	Glycerol	Diethyl ether
1	04	06	91	03
2	52	81	14	05
3	06	07	84	08
4	01	02	97	02

Conditions: catalyst dosage-0.5g, Temperature-50 °C, Molar ratio-1:3

Table 3. Effect of contact time on biodiesel synthesis over $MgAlPO_4$

Time (hr)	Conversion (%)	Selectivity (%)		
		Bio-diesel	Glycerol	Diethyl ether
1	12	13	79	09
2	25	31	67	02
3	43	44	53	02
4	05	07	91	02

Conditions: catalyst dosage-0.5g, Temperature-50 °C, Molar ratio-1:3

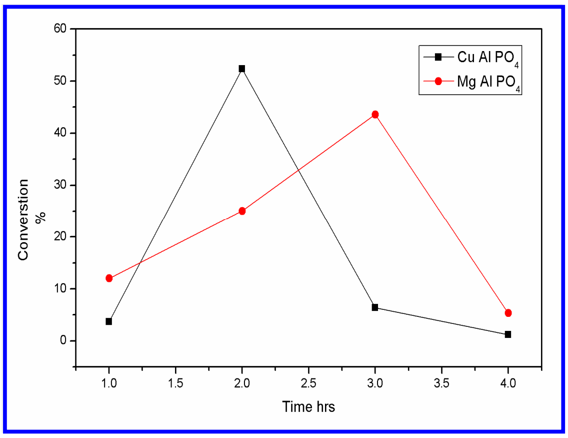

Fig. 5: Effect of contact time on biodiesel synthesis

4.2 Effect of Temperature

The percentage conversion of castor oil and selectivity of the products are studied over $CuAlPO_4$ and $MgAlPO_4$. The temperature effect on this reaction is shown in the Table 4 & 5 and *Fig*. 6.

Table 4. Effect of Temperature on biodiesel synthesis over $CuAlPO_4$

Temp (°C)	Conversion %	Selectivity (%)		
		Bio diesel	Glycerol	Diethyl ether
Room T	42	74	23	3
50	62	46	43	11
70	22	23	70	8
80	18	41	39	20

Conditions: Catalyst dosage-0.5g, Time-2hr, Molar ratio-1:3

Table 5. Effect of temperature on biodiesel synthesis over $MgAlPO_4$.

Temp (°C)	Conversion (%)	Selectivity (%)		
		Bio diesel	Glycerol	Diethyl ether
Room T	17	21	78	01
50	18	23	59	18
70	15	15	69	16
80	9.33	9.80	39.45	7.86

Conditions: catalyst dosage-0.5g, Time-2hr, Molar ratio-1:3

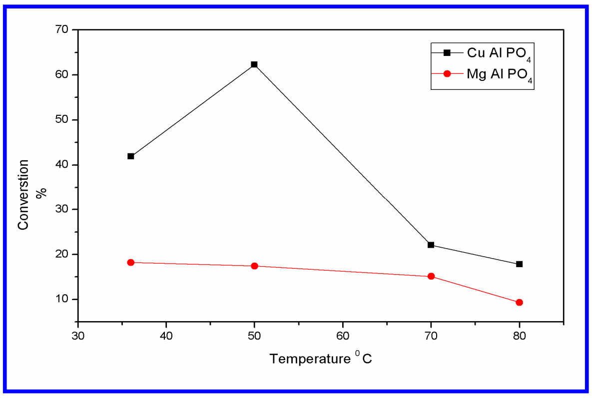

Fig. 6: Effect of contact temperature on Biodiesel synthesis

4.3 Effect of Mole ratio

The mole ratio effect of castor oil with ethanol over $CuAlPO_4$ and $MgAlPO_4$ catalyst on transesterification reaction is studied and shown in *Fig*.7. Mole ratio effect on biodiesel synthesis has been studied from 1:2 to 1:4 ratio (castor oil: ethanol). The data are given in the Table 6 & 7. With increased of ethanol ratio castor oil conversion increases upto 1:3 and further increased of mole ratio decreases the conversion. Selectivity of the biodiesel also increases with increased of mole ratio upto 1: 3 and further increased of mole ratio decreases the biodiesel selectivity.

Table 6. Effect of Mole ratio on biodiesel synthesis over $CuAlPO_4$

Mole Ratio	Conversion (%)	Selectivity(%)		
		Biodiesel	Glycerol	Diethyl ether
1:2	06	07	01	92
1:3	52	81	14	05
1:4	01	01	97	01

Conditions: Temperature-50 °C , Time-2hr, Catalyst dosage-0.5g

Table 7. Effect of Mole ratio on biodiesel synthesis over $MgAlPO_4$

Mole Ratio	Conversion %	Selectivity(%)		
		Bio-diesel	Glycerol	Diethyl ether
1:2	*02*	20	70	10
1:3	25	31	67	02
1:4	*01*	02	97	02

Conditions: Temperature-50 °C , Time-2hr, Catalyst dosage-0.5g

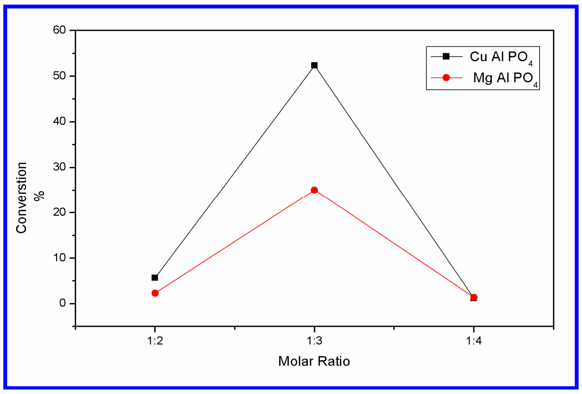

Fig. 7: Effect of Molar ratio on biodiesel synthesis

4.4 Effect of catalytic dosage

In the transesterification of castor oil with ethanol over $CuAlPO_4$ and $MgAlPO_4$, the amount of Tatsuo kimura. Microporous and catalyst used for the conversion and selectivity are studied by increasing the catalyst dosage from 0.5g to 1.5g. Experimental data are given in the Table 8 & 9 and the effect of transesterification is shown in the *Fig.8*. Conversion of the reaction decreases with increased of catalytic dosage. However, the biodiesel selectivity decrease with increased of catalytic dosage . But glycerol selectivity increases with increased of catalyst dosage. The mole ratio is fixed as 1:3. The mole ratio is sufficient for producing biodiesel at the catalyst dosage of 0.5g. When increase the catalyst dosage cleavage of

ester (castor oil) increases . Ethanol also react with catalyst and may be produced ethylene gas. So biodiesl formation is decreases with increased of catalytic dosage. It is supported by the selectivity of glycerol. The glycerol selectivty increases with increased of catalyst dosage due to the cleavage of ester linkage. The alcohol is not sufficient for transesterification reaction and hence the hydrocarbon chain of the castor oil may be cracked and evolved as the gaseous product . Hence the biodiesel conversion decreases with increased of catalyst dosage.

Table 8. Effect of catalytic dosage on biodiesel synthesis over $CuAlPO_4$

Catalytic dosage (g)	Conversion %	Selectivity(%)		
		Bio-diesel	Glycerol	Diethyl Ether
0.5	52	81	14	05
1.0	31	39	55	05
1.5	11	23	74	03

Conditions: Temperature-50 °C , Time-2hr, Molar ratio-1:3

Table 9. Effect of catalytic dosage on biodiesel synthesis over $MgAlPO_4$

Catalytic dosage (g)	Conversion (%)	Selectivity(%)		
		Biodiesel	Glycerol	Diethyl ether
0.5	25	31	67	02
1.0	13	14	84	02
1.5	06	07	92	01

Conditions: Temperature-50 °C , Time-2hr, Molar ratio-1:3

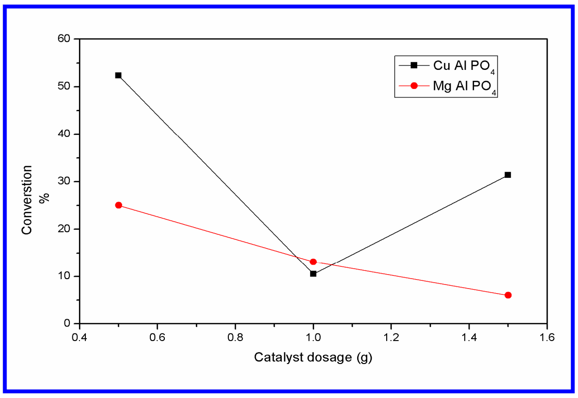

Fig. 8: Effect of Catalytic dosage on biodiesel synthesis

5. CONCLUSION

Mesoporous $CuAlPO_4$ and $MgAlPO_4$ have been successfully synthesised by adopting simple hydrothermal techniques. These synthesised materials are characterised by FT-IR, XRD, SEM, BET surface area measurements. The FT-IR spectrum proved that the formation of tetrahedral framework. XRD analysis and SEM images are confirmed the crystalline nature and the morphology of the molecular sieves. BET surface area analysis is an evidence for the higher surface area and the pore diameter of the porous materials. Thus, the characterisation techniques proved the formation of Mesoporous $MgAlPO_4$ and $CuAlPO_4$ molecular sieves. The biodiesel synthesis reaction has been carried out by using the ethanol. Conversion and selectivtity of biodiesel are more on $CuAlPO_4$ than $MgAlPO_4$.

REFERENCES

Campelo, J. M., Jaraba, M., Luna, D., Luque, R., Marinas, J. M. and Romero, A. A., Effect of phosphate precursor and rganic additives on the structural and catalytic properties of amorphous mesoporous $AIPO_4$ materials, *Chem. Mater*., 15(17), 3352-3364(2003). doi.10.1021/cm030206+

Campelo, J. M., Marinas, J. M., Mendioroz, S. and Pajares, J. A., Texture and surface chemistry of aluminium phosphates, *J. Catal*., 101(2), 484-495(1986). doi:10.1016/0021-9517(86)90275-7

Cheralathan, K., Kannan, C., Palanichamy, M. and Murugesan, V., Ethylation of tolyene over aluminophosphate based molecular sieves in the vapour phase, *Ind. J. Chem. Technol., 39A*:921-927(2000).

Elangovan, S. P., Kannan, C., Arabindoo Banumathi and Murugesan, V., Aniline methylation over AFI and AEL type molecular sieves, *Applied Catalysis A: General*, 174(1-2), 213-219(1998). doi:10.1016/S0926-860X(98)00189-6

Jing Yu, Anjie Wang, Xiang Li, Juan Tan, Yongkang Hu, An improved calcinations route to obtain high quality mesoporous aluminophosphates materials, *Mater. Lett.*, 61(13), 2620-2623(2007). doi:10.1016/j.matlet.2006.10.009

Melo, A. A. Rogerio, Giotto, M. V., Rocha, J. and Urquieta Gonzailez, E. A., MCM-41 ordered mesoporous molecular sieves synthesis and characterization, *Mater. Res*., 2(3), 173-179(1999). doi:10.1590/S1516-14391999000300010

Narasimharao, K., Lee, A. and Wilson, K., Catalysts in production of Biodiesel : A review, *Journals of Biobased Materials and Bioenergy*, 1(1), 19-30(2007). doi:10.1166/jbmb.2007.002

Selvam, P. and Mohapatra, S. K., Thermally stable trivalent iron-substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieves: Synthesis, characterization and catalytic properties, *J. Catal.*, 238(1), 88-99(2006). doi:10.1016/j.jcat.2005.12.005

Subrahmanyam, Ch., Louis, B., Rainone, F., Viswanathan, B., Renken, A. and Varadarajan, T. K., Catalytic oxidation of toluene with molecular oxygen over Cr-substituted mesoporous materials, *Applied catalysis A: General*, 241(1-2), 205-215(2003). doi:10.1016/S0926-860X(02)00469-6

Tatsuo Kimura, Surfactant – template mesporous aluminophosphate – based materials and the recent progress, *Microporous and Mesoporous Materials*, 77:97-107(2005). doi:10.1016/j.micromeso.2004.08.023

Vijayasankar, A. V., Mahadevaiah, N., Bhat, Y. S. and Nagaraju, N., Mesoporous aluminophosphate materials: influence of method of preparation and iron loading on textural properties and catalytic activity, *J. Porous Mater.*, 18(3), 369-378(2011). doi:10.1007/s10934-010-9387-z